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(54) **Polymer base blend compositions containing destructured starch.**

- (57) A thermoplastic polymer composition comprising
- a destructured starch, and
  - an effective amount of at least one polymer which contains at least two different types of functional groups, one of said types of these groups being hydroxyl groups.
- The composition may contain further conventional additives as well as hydrophobic, substantially water-insoluble polymers.

**EP 0 404 723 A2**

## Polymer base blend compositions containing destructurized starch

The present invention relates to polymer compositions capable of being formed by heat and pressure into articles having dimensional stability and enhanced physical properties, and to pre-mixes useful for preparing these compositions. These compositions and pre-mixes comprise destructurized starch and other polymers as described herein.

It is known that natural starch which is found in vegetable products and which contains a defined amount of water can be treated at an elevated temperature and in a closed volume, thereby at elevated pressures, to form a melt. The process is conveniently carried out in an injection molding machine or extruder. The starch is fed through the hopper onto a rotating, reciprocating screw. The feed material moves along the screw towards the tip. During this process, its temperature is increased by means of external heaters around the outside of the barrel and by the shearing action of the screw. Starting in the feed zone and continuing in the compression zone, the particulate feed becomes gradually molten. It is then conveyed through the metering zone, where homogenization of the melt occurs, to the end of the screw. The molten material at the tip can then be treated further by injection molding or extrusion or any other known technique to treat thermoplastic melts, to obtain shaped articles.

This treatment, which is described in the European Patent Application No. 84 300 940.8 (Publication No. 118 240) which patent is incorporated herein by reference, yields an essentially destructurized starch. As described in the above mentioned patent, the reason for this is that the starch is heated above the glass transition and the melting temperatures of its components. As a consequence, a melting and disordering of the molecular structure of the starch granules takes place, so that an essentially destructurized starch is obtained. The expression "destructurized starch" defines starch obtained by such thermoplastic melt formation. Reference is also made to European Patent Applications No. 88810455.1 (Publication No. 298,920), No. 88810548.3 (Publication No. 304,401) and No. 89810046.6 (Publication No. 326,517) which further describe destructurized starch, methods for making it, and uses of it. These application are also incorporated herein by reference.

It is preferred that the destructurized starch used in the present invention has been heated to a high enough temperature and for a time long enough so that the specific endothermic transition analysis as represented by differential scanning calorimetry (DSC) indicates that a specific relatively narrow peak just prior to oxidative and thermal degradation has disappeared, as described in the above-mentioned European Patent Application No. 89810046.6 (Publication No. 326 517).

Destructurized starch is a new and useful material for many applications. An important property is its biodegradability. In humid air, however, destructurized starch takes up water from the air, thereby increasing its moisture content. As a consequence, a shaped article made from destructurized starch may under such conditions lose its dimensional stability. On the other hand such an article may dry out in low humidity and become brittle.

Thermoplastic starch has unique properties and while these are very useful, they may limit its utility in cases where a softer, more resilient or harder, tougher polymer is desired.

Thermoplastic starch as mentioned can be extruded and molded into numerous useful shapes and profiles. However, the processing parameters such as water content, temperature, and pressure are generally critical and must be narrowly controlled to achieve reproducible quality products. This is a further disadvantage for many applications.

To overcome these potential limitations, it would be useful to increase the dimensional stability over a wide humidity range; to increase the toughness (measured as break energy); to increase the elasticity (measured as elongation); to decrease polymer stiffness (measured as Young's modulus) and increase the hardness.

Broadening processing latitude increases the variety of shapes and composites and decreases the need for close controls. It would therefore also be useful to improve the control of the melt strength, e.g. increasing the processing latitude for extruding, injection molding, film blowing or fiber drawing and to control the surface tack and adhesion to other substrates.

Conventional thermoplastic materials are hydrophobic, substantially water-insoluble polymers which are conventionally processed in the absence of water and volatile materials. Starch to the contrary forms a melt in the presence of water but decomposes at elevated temperature, i.e. around 240°C. It was therefore expected that such a starch melt could not be used as a thermoplastic component together with hydrophobic, substantially water-insoluble polymeric materials not only because starch forms a melt in the presence of water as described above, but also because of its chemical structure and hydrophilic nature.

It has now been found that starch, when heated in a closed volume at proper moisture and temperature

conditions, as described above, to form a melt of destructured starch, is substantially compatible in its processing with melts formed by hydrophobic substantially water insoluble thermoplastic polymers and that the two types of molten materials show an interesting combination of properties, especially after the melt has solidified.

5 One very important aspect is the surprisingly improved dimensional stability of such destructured starch blended with such hydrophobic thermoplastic materials. Such polymer compositions are described in copending European Patent Application No. 89810078.9 (Publication No. 327,505) which is incorporated herein by reference. Although articles made from such compositions possess better dimensional stability than those made from destructured starch alone, the physical properties of the therein-described  
10 compositions are not as good as might be desired for some end uses. In particular, it is important that articles made from destructured starch compositions retain sufficient strength and dimensional stability to perform their desired function while still being biodegradable after disposal.

It has now been found that articles made from such destructured starch blended with specific hydrophobic thermoplastic materials as described herein show a surprising increase in all or a part of their  
15 physical properties and behaviour of their melts as to overcome the limitations as explained above. Moreover it was surprisingly found that many of the blends described herein show a significantly improved dimensional stability in humid air compared with non-blended destructured starch whilst retaining a surprisingly high degree of disintegration in contact with moisture water which in consequence leads to a high degree of biodegradability.

20 In order to achieve such properties, it has been found useful to make polymer compositions comprising: a) destructured starch, b) at least one polymer which contains at least two different types of functional groups, one of said types being hydroxyl groups (referred to herein as "component b"), and optionally c) a substantially water-insoluble polymer different from those defined as component b). In one aspect, the present invention relates to a composition comprising destructured starch and component b). This  
25 composition is useful itself for making finished articles, but it is primarily useful as a "pre-mix" for combining with the substantially water-insoluble polymer. In a second aspect, the invention comprises the ternary composition of destructured starch, component b), at least one substantially water-insoluble polymer (component c)). These compositions may be in the form of powdery mixtures of the components, melts, or solid forms. The invention also includes methods for making and using both above-described  
30 compositions and shaped articles made therefrom.

The compositions of the first aspect of the invention comprise:

a) destructured starch, and  
b) at least one polymer which contains at least two different types of functional groups, one of said types being hydroxyl groups.

35 Such polymer composition may optionally contain further additives.

Specifically, the first aspect of the present invention is a polymer composition capable of being formed into articles having substantial dimensional stability comprising:

a) destructured starch, and  
b) at least one polymer which contains at least two different types of functional groups, one of said  
40 types being hydroxyl groups; said polymer being present in an amount effective to enhance the physical properties of said articles (which amount is sometimes referred to herein as an "effective amount" of component b).

Preferably this polymer composition additionally comprises at least one component c):

c) a substantially water-insoluble thermoplastic polymer which does not fall within the definition of  
45 those compounds defined herein as component b).

The present invention includes said polymer compositions in the form of powdery mixtures of their components, in the form of melts, or in solidified form.

Component b) is chosen as described herein to be substantially compatible with the starch and also to promote the compatibility of component c) with the combination of starch and component b).

50 The present invention further refers to a method of producing said polymer compositions in the molten or solid form as well as a method of producing shaped articles from said polymer compositions, and to the resulting shaped articles made therefrom.

The polymer compositions of the present invention are prepared by admixing destructured starch, component b), and optionally component c) and any further additives. This mixture is then heated in a closed volume to elevated temperatures until a homogeneous melt is obtained, and shaped articles can be  
55 formed therefrom.

An alternate method of producing the polymer compositions of the present invention comprises: Heating starch, which is in a condition to be destructured, in a closed volume to elevated temperatures and at

elevated pressures for a time sufficient to destructure the starch and form a melt; adding component b) as well as other polymers and/or additives before, during or after such starch destructure; and continuing to heat the mixture until a homogenous melt is obtained. It is preferred that component b) and, if desired, component c), as well as other additives be combined with the starch and the combination formed into a melt. The starch in this combination may be already wholly or partially destructure or the destructure may take place during melt formation.

The present invention further refers to the process of working said polymer composition under controlled water content, temperature and pressure conditions as a thermoplastic melt wherein said working process is any known process, such as, for example injection molding, blow molding, extrusion, coextrusion, compression molding, vacuum forming, thermoforming or foaming. All of these processes are collectively referred to herein as "forming".

The term "functional group" as used herein includes all known polar groups that may be bound to the polymer chain such as, for example, hydroxy, alkoxy, carboxy, carboxyalkyl, alkyl carboxy, halo, pyrrolidono, acetal, and the like. These groups should be selected from those which will not degrade the starch.

The term "starch" as used herein includes chemically substantially non-modified starches as for example carbohydrates of natural, vegetable origin, composed mainly of amylose and/or amylopectin. They can be extracted from various plants, examples being potatoes, rice, tapioca, corn (maize), pea, and cereals such as rye, oats and wheat. Preferred is starch made from potatoes, corn, wheat or rice. Mixtures of starch obtained from these sources are contemplated. It further includes physically modified starches such as gelatinized or cooked starches, starches with a modified acid value (pH), e.g. where acid has been added to lower their acid value to a range of about 3 to about 6. Further included are starches, e.g. potato starch, in which the divalent ions like  $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$ -ions associated with the phosphate groups have been partially or completely washed out from the starch or optionally wherein the ions present in the starch have been replaced partially or wholly by the same or different mono- or polyvalent ions. It further includes pre-extruded starches, as described in the above-referenced European Patent Application No. 88810548.3 (Publication No. 304,401).

As described above, it has been found that starches, e.g. with a water content within the range of about 5 to about 40% by weight based on the weight of the composition, undergo a specific narrow endothermic transition on heating to elevated temperatures and in a closed volume just prior to the endotherm change characteristic of oxidative and thermal degradation. The specific endothermic transition can be determined by differential scanning calorimetric analysis (DSC) and is indicated on the DSC-diagram by a specific relatively narrow peak just prior to the endotherm characteristic of oxidative and thermal degradation. The peak disappears as soon as the mentioned specific endothermic transition has been undergone. The term "starch" includes also treated starches wherein said specific endothermic transition has been undergone. Such starch is described in the EP 89810046.6 (Publication No. 326,517).

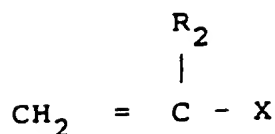
Although at the current time, destructure of starch requires the presence of water in ranges disclosed herein, the present inventive compositions also contemplate the use of destructure starch prepared by other methods, e.g. without the use of water.

The water content of such a starch/water composition is preferably about 5 to about 40 % water by weight of the starch/water component and preferably about 5 to about 30 %. However, in order to work with the material near its equilibrium water content to which it gets when it is finally exposed to the free atmosphere, a water content of about 10 to about 22 %, preferably of about 14 to about 18 % by weight calculated based on the starch/water component should be used in processing and is preferred.

The polymer of component b) is preferably a polymer containing vinyl alcohol units. More preferably component b) is a poly(vinyl ester) wherein the ester groups are partially hydrolyzed or a copolymer containing vinyl alcohol units as well as other units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate, with monomers such as ethylene, vinyl chloride, vinyl ethers, acrylo-nitrile, acryl amide, omega-octadecene, vinyl-butyl ether, vinyl-octadecyl ether, vinyl pyrrolidone and other known monomers, with subsequent hydrolysis of at least some of the vinyl-ester groups.

These polymers of component b) have preferably from about 20 to about 99 mol % hydroxyl containing units such as vinyl alcohol units, preferably from about 30 to about 99 mol % and most preferably from about 40 to about 95 mol % of the hydroxyl containing unit, the remaining units being as mentioned above.

In addition component b) can be a polymer or copolymer as obtained from polymerizing or copolymerizing monomers of the formula:



5

wherein R<sub>2</sub> is hydrogen or methyl; and X is an organic moiety with up to 8 carbon atoms substituted by 1 to 3 hydroxyl groups and/or containing 1 or 2 carboxylate groups; and does not form a vinyl alcohol.

Such X can be exemplified by the moiety X<sub>1</sub> wherein X<sub>1</sub> is -CH<sub>2</sub>OH, -O-CH<sub>2</sub>-CH<sub>2</sub>-OH, -C(O)OCH<sub>2</sub>-CH<sub>2</sub>OH or -C<sub>6</sub>H<sub>4</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>OH.

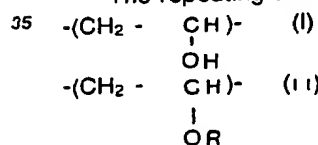
Component b) may also be an ester derivative of maleic acid or fumaric acid which optionally contain hydroxyl groups, such as  
HOCH<sub>2</sub>-CH<sub>2</sub>-O(O)C-HC = HC-C(O)O-CH<sub>2</sub>-CH<sub>2</sub>OH  
(cis or trans)

The monomers of the compounds of formula CH<sub>2</sub> = C(R<sub>2</sub>)X or said derivatives of maleic or fumaric acid may be copolymerized with vinyl esters, preferably vinyl acetate and/or with monomers such as ethylene, vinyl chloride, vinyl ethers, acrylic acid esters, acrylonitrile, methacrylic acid esters, maleic acid esters, acryl amide, omega-octadecene, vinyl butyl ether, vinyl-octadecyl ether, vinyl pyrrolidone and other known monomers. Such polymers and copolymers are known.

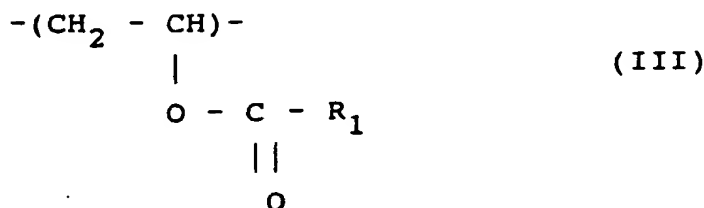
It is preferred that the polymer does not contain hydroxyl groups together with carboxyl groups bound directly to the same main polymer chain because crosslinking may occur prior to or during processing. However, this does not necessarily always happen and such useful combinations are included within the scope of the present invention.

The amount of hydroxyl containing monomer will depend on the type of copolymer used carrying the other functional group. The preferred molar ratios are given above and are generally applicable. However, if the monomer carrying the functional group which is not hydroxyl has an elevated molecular weight compared to the hydroxyl carrying moiety, then a higher proportion of the latter moiety will be required. In this sense it is recommended that the weight % of the hydroxyl moiety (-OH) is from 4.5 to 35 and preferably from 9.0 to 25 weight percent of the component b). If the monomer carries a hydroxyl and at the same time another functional group e.g. an ester group no comonomer may be needed because the homopolymer carries two different functional groups. It is no problem to the person skilled in the art to optimize component b), e.g. by combining different molar ratios of known monomers or combining other monomers than indicated here. Many of these polymers and copolymers are known.

The repeating units in the polymer of component b) can be exemplified by the following formulas:



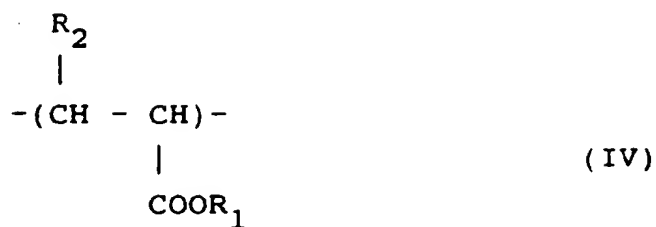
R = preferably methyl, ethyl, propyl, butyl, octadecyl



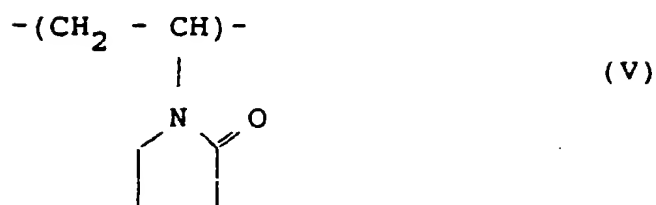
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R<sub>1</sub> = is a saturated or unsaturated C<sub>1</sub>-C<sub>21</sub>- hydrocarbon, preferably methyl, ethyl, propyl, butyl

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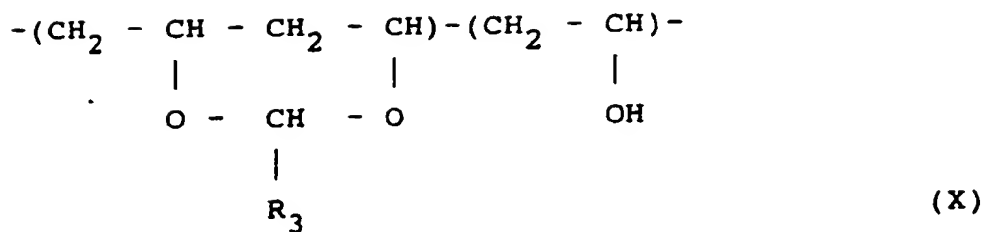
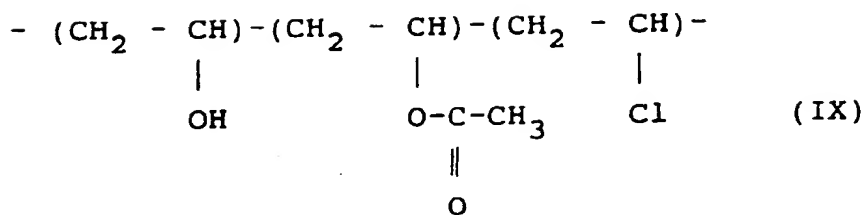
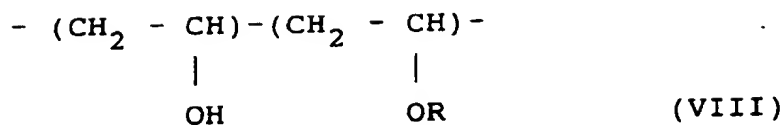
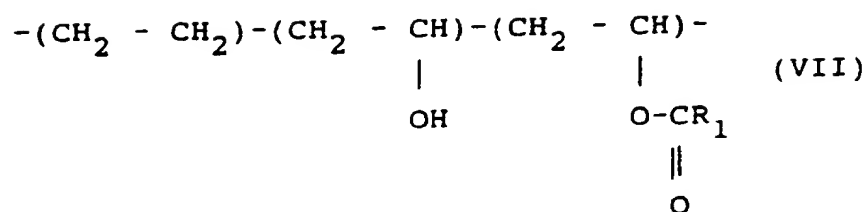
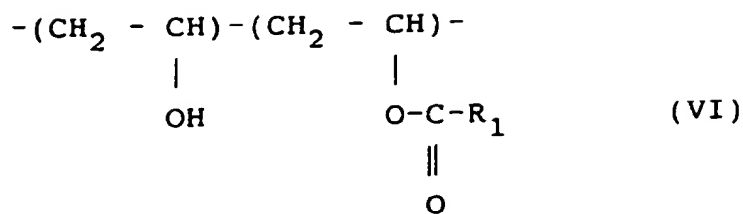


10  $R_2 = H, CH_3$

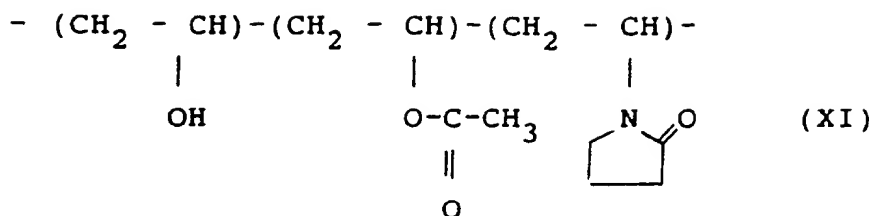


20 The polymers of component b) may have a general formula wherein the number of repeating units varies for each individual type of copolymer and is known per se as e.g. described in "Encyclopaedia of Polymer Science and Technology, Interscience Publ. Vol. 14, 1971." These copolymers may be described by the following general formulas incorporating the mer units described above. The units within the brackets represent the individual mer units within each copolymer. These units may be combined in any known  
 25 fashion, including random or block copolymerization. The molecular weight of the copolymer may be within known ranges.





R<sub>3</sub>: H, a saturated or unsaturated C<sub>1</sub>-C<sub>21</sub>- hydrocarbon, preferably H, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>



Preferred copolymers of the component b) are those which can be described as containing vinyl alcohol (I) units together with vinyl ether (II) and/or vinyl ester (III) units. Such copolymer types correspond to compounds of the formulas (VI) to (X) from which compounds of the formulas (VI), (VII) and (VIII) are preferred.

These preferred copolymers of component b) are copolymers as obtained by polymerization of a vinyl ester with one or more monomers selected from the group consisting of ethylene, vinyl ethers, with subsequent hydrolysis of at least some of the vinyl ester groups.

Such preferred copolymers of component b) are e.g. polyvinylalcohol-co-vinyl-acetate; ethylene/ vinyl alcohol/vinyl acetate copolymers; ethylene/ vinyl chloride/vinyl alcohol/vinyl acetate graft copolymers; vinyl alcohol/vinyl acetate/vinyl chloride copolymers; vinyl alcohol/vinyl acetate/vinyl chloride/ diacryl amide copolymers; vinyl alcohol/vinyl butyral copolymers; vinyl alcohol/vinyl acetate/ vinyl pyrrolidone copolymers; vinyl alcohol/ styrene copolymers. Combinations or mixtures of these copolymers are included within the scope of component b).

As mentioned above, the polymer composition comprising the components a) and b) optionally contains one or more essentially water-insoluble hydrophobic polymers (component c), as well as further additives.

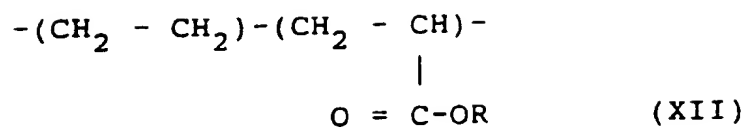
The component c) is an essentially water-insoluble polymer or a mixture of such essentially water-insoluble polymers. Component c) is preferably present in an amount effective to enhance the physical properties of articles made from the composition of the invention (which amount is sometimes referred to herein as an "effective amount" of component c)).

As used herein an "essentially water-insoluble thermoplastic polymer" is a polymer which preferably absorbs water at a rate of less than 10 %, preferably less than 5 % per 100 grams of the polymer at room temperature and preferably at a rate of less than 2 % per 100 grams of the polymer at room temperature.

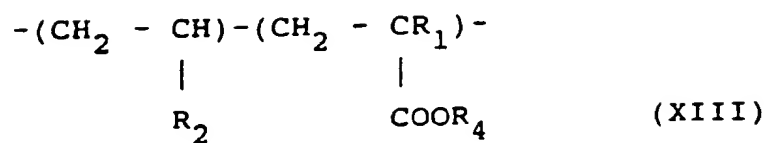
Examples of essentially water-insoluble thermoplastic materials are polyolefines, such as polyethylene (PE), polyisobutylenes, polypropylenes; vinyl polymers such as poly(vinyl chloride) (PVC), poly(vinyl acetates); polystyrenes; polyacrylonitriles (PAN); poly(vinyl carbazoles) (PVK); essentially water-insoluble polyacrylates or polymethacrylates; polyacetals; thermoplastic polycondensates such as polyamides (PA), polyesters, polyurethanes, polycarbonates, poly(alkylene terephthalates); polyarylethers and thermoplastic polyimides; and high molar-mass, essentially water-insoluble or crystallizable poly(alkylene oxides) such as polymers of ethylene oxide and propylene oxide as well as their copolymers.

Further included are essentially water-insoluble thermoplastic copolymers known such as alkylene/vinyl ester-copolymers preferably ethylene/vinyl acetate-copolymers (EVA); ethylene/vinyl alcohol-copolymers (EVAL); alkylene/acrylates or methacrylate copolymers preferably ethylene/acrylic acid-copolymers (EAA); ethylene/ethyl acrylate-copolymers (EEA); ethylene/methyl acrylate-copolymers (EMA); ABS- copolymers; styrene/acrylonitrile-copolymers (SAN); alkylene/maleic anhydride copolymer preferably ethylene/maleic anhydride copolymer; partially hydrolyzed polyacrylates or polymethacrylates; partially hydrolyzed copolymers of acrylates and methacrylates; acrylic acid esters/acrylonitrile copolymers and hydrolysates thereof; acrylamide/acrylonitrile copolymers; and mixtures thereof.

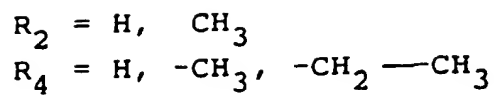
Further, copolymers useful as a component c) are exemplified hereinbelow schematically by the following general formulas. The units within brackets represent the individual component mer units within each copolymer. These units may be combined in any known fashion, including random or block copolymerization, and the molecular weight of the polymer may be within known ranges.



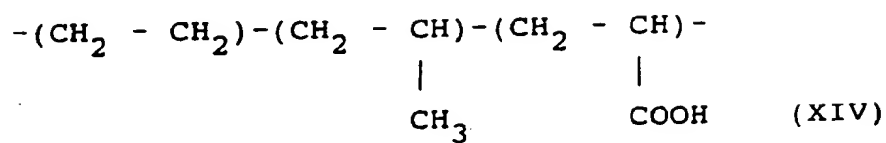
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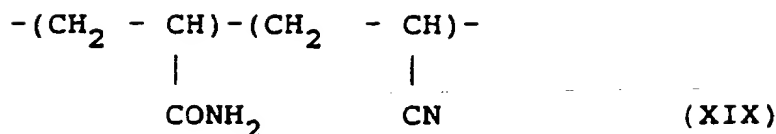
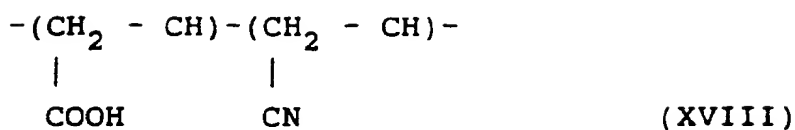
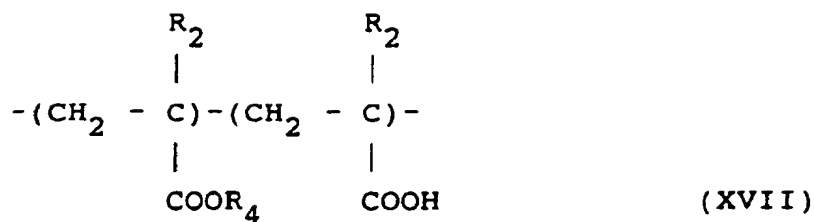
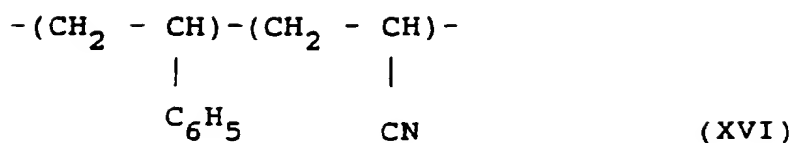
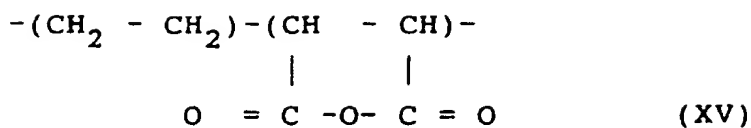
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Preferred from these are those which undergo melt formation at a set processing temperature preferably within the range of 95°C to 240°C, preferably within the range of 95°C to 220°C and more preferably within the range of 95°C to 190°C.

Preferred from these are further those polymers containing polar groups such as ether, acid, ester, amide, or urethane groups. Such polymers include e.g. copolymers of ethylene, propylene or isobutylene with vinyl compounds or acrylates such as ethylene/vinyl acetate-copolymers (EVA), ethylene/vinyl alcohol-copolymers (EVAL), ethylene/acrylic acid-copolymers (EAA), ethylene/ethyl acrylate-copolymers (EEA).

ethylene/methacrylate- copolymers (EMA), styrene/acrylonitrile-copolymers (SAN); polyacetals; block copolymers of amide-ethers, amide-esters; block copolymers of urethane-ethers, urethane-esters; as well as their mixtures.

Most preferred are those polymers containing one type of functional group which is the same type of functional group as that of component b) which is not hydroxyl.

Such essentially water-insoluble thermoplastic polymers may be added in any desired amount as described herein.

Such polymers may be used in any known form. Their molecular weight is also generally known in the art. It is also possible to use such polymers of relatively low molecular weight (oligomers). Which molecular weight to chose is a matter of optimization and known to the one skilled in the art.

In the composition according to this invention, the two components a) and b) or the three components a), b) and c) always add up to 100 % and the values of the components (in %) given hereinbelow refer to this sum of 100 %.

The ratio of destructured starch to the component b) and optionally to the sum of the components b) and c) can be 1:99 to 99:1. It is however preferred that the destructured starch contributes noticeably to the properties of the final material. Therefore, it is preferred that the destructured starch is present in an amount of at least 20%, more preferably 50% and most preferably in the range of 70% to 99% by weight of the entire composition. That is, component b) is and optionally the sum of the components b) and c) are present in amounts of about 80% or less, more preferably less than or equal to 50% and most preferably in the range of 30% to 1% by weight of the entire composition.

Component b) is a relatively polar material. When it functions in the present compositions in combination with component c), it is able to mix more readily with a more polar component c) than with a less polar one. Accordingly, with more polar components c), relatively less of component b) will be required than with less polar ones. The skilled worker will be able to select appropriate ratios of components b) and c) to obtain a substantially homogenous melt composition.

A mixture of 1 to 15% by weight of the components b) or optionally of the sum of the components b) and c) and 99 to 85% of the destructured starch shows already a significant improvement in the properties of the obtained materials. For certain applications a ratio of said components b) or optionally of the sum of the components b) and c) to the destructured starch component of 1-10% to 99-90% by weight is preferred. If the destructured starch contains water, the percentage of this destructured starch component is meant to be the destructured starch/water component, i.e. including the weight of water.

The starch may be mixed with the additives as named hereinbelow to yield a free flowing powder useful for continuous processing and is destructured and granulated before it is mixed with the components b) and optionally c) or the other optionally added components. The other components to be added are preferably granulated to an equal granular size as the granulated destructured starch.

However, it is possible to process native starch or pre-extruded and/or destructured granulated or powdered starch together with powdered or granulated additives and/or the polymeric material in any desired mixture or sequence.

Thus, it is preferred that the components a), b) and c) and the additives be mixed in a conventional mixer. This mixture can then be passed through an extruder to produce granulates or pellets as one form of shaped articles useful for further processing. However, it is possible to avoid granulating and to process the obtained melt directly using down-stream equipment to produce films, blown films included, sheets, profiles, pipes, tubes, foams or other shaped articles. The sheets can be used for thermoforming.

It is preferred that the fillers, lubricants and/or plasticizers are added to the starch before destructured while the addition of the coloring agents as well as of the components b), c) and the other additives can be added before, during or after destructured.

The essentially destructured starch/water component or granules have a preferred water content in the range of about 10 to 22 % by weight of the starch/water component, preferably 12 to 19% and especially 14 to 18% by weight of the starch/water component.

The water content described above refers to the percentage of water relative to the weight of the starch/water component within the total composition and not to the weight of the total composition itself, which would include also the weight of any added essentially water-insoluble thermoplastic polymer.

In order to destructure the starch and/or to form a melt of the new polymeric composition according to this invention, it is suitably heated in a screw and barrel of an extruder for a time long enough to effect destructured and melt formation. The temperature is preferably within the range of 105 °C to 240 °C, more preferably within the range of 130 °C to 190 °C depending on the type of starch used. For this destructured and melt formation, the composition is heated preferably in a closed volume. A closed volume can be a closed vessel or the volume created by the sealing action of the unmolten feed material as

happens in the screw and barrel of injection molding or extrusion equipment. In this sense the screw and barrel of an injection molding machine or an extruder is to be understood as being a closed vessel. Pressures created in a closed vessel correspond to the vapour pressure of water at the used temperature but of course additional pressure may be applied and/or generated as normally occurs in a screw and barrel. The preferred applied and/or generated pressures are in the range of pressures which occur in extrusion and are known per se, e.g. from  $5$  to  $150 \times 10^5$  N/m<sup>2</sup> preferably from  $5$  to  $75 \times 10^5$  N/m<sup>2</sup> and most particularly from  $5$  to  $50 \times 10^5$  N/m<sup>2</sup>. If the thus-obtained composition is just destructurized starch, it may be granulated and ready to be mixed with the further components according to a chosen mixing and processing procedure to obtain the granular mixture of the destructurized starch/polymer starting material to be fed to the screw barrel.

However, the obtained melt in the screw and barrel may be e.g. injection molded directly into a suitable mold, i.e. directly further processed to a final product if all necessary components are already present.

Within the screw, the granular mixture obtained as described above is heated to a temperature which is generally within the range of about  $80^\circ\text{C}$  to  $240^\circ\text{C}$ , preferably within the range of about  $120^\circ\text{C}$  to  $220^\circ\text{C}$  and especially within the range of about  $130^\circ\text{C}$  to  $190^\circ\text{C}$ . Preferably, such mixture is heated to a sufficiently high temperature and for a time long enough until the endothermic transition analysis (DSC) indicates that the specific relatively narrow peak just prior to the endotherm characteristic of oxidative and thermal degradation of starch has disappeared.

The minimum pressures under which the melts are formed correspond to the water vapour pressures produced at said temperatures. The process is carried out in a closed volume as explained above, i.e. in the range of the pressures which occur in extrusion or molding processes and known per se, e.g. from zero to  $150 \times 10^5$  N/m<sup>2</sup> preferably from zero to  $75 \times 10^5$  N/m<sup>2</sup> and most particularly from zero to  $50 \times 10^5$  N/m<sup>2</sup>.

When forming a shaped article by extrusion the pressures are preferably as mentioned above. If the melt according to this invention is, e.g., injection molded, the normal range of injection pressures used in injection molding is applied, e.g. from  $300 \times 10^5$  N/m<sup>2</sup> to  $3000 \times 10^5$  N/m<sup>2</sup> and preferably from  $700 \times 10^5$  to  $2200 \times 10^5$  N/m<sup>2</sup>.

Accordingly, the present invention provides a thermoplastic destructurized-starch substantially homogenous melt formed by the process comprising:

- 1) providing a mixture comprising starch and at least one polymer which contains at least two different types of functional groups, one of said types being hydroxyl groups (component b); and
- 2) heating said mixture in a closed volume under sufficient temperature and pressure for a time long enough to effect destructurization of said starch and form said melt.

The present invention also provides a thermoplastic destructurized-starch product having substantial dimensional stability formed by the process comprising:

- 1) providing a mixture comprising starch and at least one polymer which contains at least two different types of functional groups, one of said types being hydroxyl groups (component b);
- 2) heating said mixture in a closed volume under sufficient temperature and pressure for a time long enough to effect destructurization of said starch and form a substantially homogenous melt;
- 3) shaping said melt into an article; and
- 4) allowing said shaped article to cool to a substantially dimensionally stable thermoplastic product.

The mixture provided in step 1) of either above-described processes may additionally contain component c) and additives as described herein.

Various hydrophilic polymers may be used as additives. These include water-soluble and water-swelling polymers. As such it includes animal gelatin, vegetable gelatins resp. proteins such as sunflower protein, soybean proteins, cotton seed proteins, peanut proteins, rape seed proteins, acrylated proteins; water-soluble polysaccharides, alkylcelluloses, hydroxyalkylcelluloses and hydroxyalkylalkylcelluloses, such as:

methylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxyethylmethylcellulose, hydroxypropylmethylcellulose, hydroxybutylmethylcellulose, cellulose esters and hydroxyalkylcellulose esters such as:

cellulose acetate (CAP), Hydroxypropylmethylcellulose (HPMCP); carboxyalkylcelluloses, carboxyalkyl-alkylcelluloses, carboxyalkylcellulose, analogous known polymers made from starch; carboxymethylcellulose and their alkalimetal salts; water-soluble or water-swelling synthetic polymers such as: polyacrylic acids and polyacrylic acid esters, polymethacrylic acids and polymethacrylic acid esters, polyvinylalcohols, polyvinylacetatephthalates (PVAP), polyvinylpyrrolidone, polycrotonic acids; polyitaconic acid, polymaleic acid; suitable are also phthalated gelatin, gelatin succinate, crosslinked gelatin, shellac, cationically modified acrylates and methacrylates possessing, for example, a tertiary or quaternary amino group, such as the diethylaminoethyl group, which may be quaternized if desired; and other similar

polymers.

Preferred are synthetic polymers, most preferred are synthetic polymers such as polyacrylic acids, polyacrylic acid esters, polymethacrylic acids, polymethacrylic acid esters, polyvinyl alcohols, polyvinyl pyrrolidone.

5 Such hydrophilic polymers may optionally be added up to 50 % based on the starch/water component, preferably up to 30 % and most preferably between 5% and 20% based on the starch/water component. If any hydrophilic polymer is added, its mass should be considered along with the starch in determining the appropriate amount of water in the composition.

10 Other useful additives may be e.g. adjuvants, fillers, lubricants, mold release agents, plasticizers, foaming agents, stabilizers, coloring agents, pigments, extenders, chemical modifiers, flow accelerators, and mixtures thereof.

Examples for fillers are inorganic fillers, such as the oxides of magnesium, aluminum, silicon, titanium, etc. preferably in a concentration in the range of about 0.02 to 50 % by weight preferably 0.20 to 20 % based on the total weight of all the components.

15 Examples for lubricants are stearates of aluminum, calcium, magnesium and tin as well as talc, silicones, etc. which may be present in concentrations of about 0.1 - 5% preferably at 0.1 - 3% based upon the weight of the total composition.

Examples of plasticizers include low molecular poly(alkylene oxides), such as poly(ethylene glycols), poly(propylene glycols), poly(ethylene-propylene glycols); organic plasticizers of low molar masses, such as 20 glycerol, pentaerythritol, glycerol monoacetate, diacetate or triacetate; propylene glycol, sorbitol, sodium diethylsulfosuccinate, etc., added in concentrations ranging from 0.5 to 35%, preferably ranging from 0.5 to 10 % based on the total weight of all the components. Examples of colouring agents include known azo dyes, organic or inorganic pigments, or colouring agents of natural origin. Inorganic pigments are preferred, such as the oxides of iron or titanium, these oxides, known per se, being added in concentrations ranging 25 from 0.001 to 10%, preferably 0.5 to 3%, based on the weight of all the components.

There may further be added compounds to improve the flow properties of the starch material such as animal or vegetable fats, preferably in their hydrogenated form, especially those which are solid at room temperature. These fats have preferably a melting point of 50 °C or higher. Preferred are triglycerides of C<sub>12</sub> -, C<sub>14</sub> -, C<sub>16</sub> -, and C<sub>18</sub> - fatty acids.

30 These fats can be added alone without adding extenders or plasticizers.

These fats can advantageously be added alone or together with mono- and/or diglycerides or phosphatides, especially lecithin. The mono- and diglycerides are preferably derived from the types of fats described above, i.e. from C<sub>12</sub> -, C<sub>14</sub> -, C<sub>16</sub> -, and C<sub>18</sub> - fatty acids.

35 The total amount of fats, mono-, diglycerides and/or lecithins used are up to 5% and preferably within the range of about 0.5 to 2% by weight of the total weight of starch and any added hydrophilic polymer.

The materials may further contain stabilizers, such as antioxidants, e.g. thiobisphenols, alkyliden-bisphenols secondary aromatic amines; light stabilizers such as UV-absorbers and UV-quenchers; hydroperoxide decomposer; free-radical scavengers; stabilizers against microorganisms.

40 The compositions of the invention form thermoplastic melts on heating and in a closed volume, i.e. under conditions of controlled water-content and pressure. Such melts can be processed just like conventional thermoplastic materials, using, for example, conventional apparatus for injection molding, blow molding, extrusion and coextrusion (rod, pipe and film extrusion), compression molding, foaming, to produce known articles. The articles include bottles, sheets, films, packaging materials, pipes, rods, laminated films, sacks, bags, pharmaceutical capsules, granules, powders or foams. For example, these 45 compositions may be used to prepare low density packaging materials (e.g. foams) by well-known methods. Conventional blowing agents may be utilized if desired or, for certain compositions, the water itself may act as the blowing agent. Open cell and closed cell foams may be produced as desired by varying the composition and processing conditions. These foams produced from the present compositions will demonstrate improved properties (e.g., dimensional stability, moisture resistance, etc.) when compared with 50 foams made of starch without incorporation of the components b) and c) according to this invention.

These compositions may be used as carrier materials for active substances, and may be mixed with active ingredients such as pharmaceuticals and/or agriculturally active compounds such as insecticides or pesticides for subsequent release applications of these ingredients. The resulting extruded materials can be granulated or worked to fine powders.

55 The following examples are provided to further explain and exemplify the invention but not to limit the scope thereof, which scope is defined by the appended claims.

Example 1

(a) 5000 g of potato starch containing 14.87 % water were placed in a high speed mixer and 485 g of water were added under stirring. To the above mixture of starch and water, 425 g of polyvinyl alcohol-co-vinyl acetate, (component b)) containing 11 % - 13 % of the monomeric units as vinyl acetate and 87 % - 89 % of the monomeric units as vinyl alcohol sold as Airvol 540S by Air Products; and 42 g of polyethylene-co- vinyl acetate (component c)) containing 80 % of the monomeric units as ethylene and 20 % of the monomeric units as vinyl acetate sold as Escorene UL02020 by Exxon; 42.5 g of hydrogenated fat (lubricant/release agent) sold as Boeson VP by Boehringer Ingelheim; 21.25 g of a melt flow accelerator (lecithin) sold as Metarin P by Lucas Meyer and 21.25 g of titanium dioxide (pigment and solid mixture flow accelerator) were added under stirring. The water content of the final mixture was 19.98 %.

(b) 5000 g of the mixture prepared under (a) were fed through a hopper into a Leistritz Single Screw Lab Extruder LSM 30 having a temperature profile of 55 °C/ 145 °C/ 165 °C/ 165 °C. The screw speed was 50 rpm. The output of extrudate was 124 g/min.

The extrudate was cut into granulates and stored for further processing.

(c) For further processing the granulates were conditioned to a water content of 17 % by adding water under stirring in a conventional mixer. The obtained material was then fed through a hopper to a Kloeckner-Ferromatic FM 60 injection-molding machine, for the production of tensile test pieces. The temperature profile was 90 °C, 155 °C, 155 °C, 155 °C, the screw speed: 180 rpm, the shot weight 8.2 g, the residence time 450 sec., the injection pressure 1800 bar, the back pressure 30 bar.

All tensile test pieces were conditioned in a climatic cabinet at 50 % R.H. for five days as an arbitrary standard condition.

The test pieces were of standard DIN design (DIN No. 53455).

(d) The conditioned tensile test pieces were then tested for their stress/strain behaviour on an Instron tensile test apparatus, each test with 4 pieces.

The samples were measured at room temperature using an extension rate of 10 mm per minute. Results are presented in Table 1 and compared with those obtained with tensile test pieces obtained from the same starch processed in a similar way but in absence of components b) and c). It can be seen from the results that the Young's modulus of the ternary blend is decreased from 1.56 to 1.29 showing a softening of the injection molded blend material compared to similar tensile test pieces, produced from unblended starch.

The break stress goes from 32.72 MPa to 37.22 MPa indicating an increase of the strength of the blend. The break strain (elongation at break) going from 15.82 % to 33.33 % and break energy from 194.30 kJ/m<sup>2</sup> to 415.75 kJ/m<sup>2</sup> showing a considerable increase in the toughness of the blend material over the unblended one.

Table 1

	Break Strain	Break Energy
	(%)	(kJ/m <sup>2</sup> )
starch (unblended starch)	15.82	194.3
ternary blend Example 1	33.33	415.75

Of course different blend compositions show different values for the physical parameters indicated. To obtain the best values is a matter of optimization by varying the concentration of the different components, which is no problem to the expert in the art.

Example 1 is repeated with the following blends as per the Examples 2 to 10 whereby analogous results as given in Table 1 are obtained.

Example 2

Example 1 is repeated except that the ratio of the components is varied as given in Table 2. For comparison perspective, Example 1 is shown as Blend No. 1.



Table 2

Blend No.	starch: component b) + c) (weight ratio)	component b): component c) (weight ratio)
2	50 : 50	100 : 0
3	60 : 40	99 : 1
4	70 : 30	50 : 1
5	80 : 20	20 : 1
Ex.1	91.5 : 8.5	10 : 1
6	90 : 10	1 : 1
7	94 : 6	1 : 10
8	98 : 2	1 : 50
9	99 : 1	1 : 99

The resulting injection molded polymers are tougher and more resistant to humid air than the unmodified starch polymer. The toughness as judged by resistance to breaking upon bending increases from blend 9 to blend 2 in concert with the combined increase in vinyl alcohol content. While the resistance to softening in humid atmosphere is improved in all cases relative to unmodified starch, the resistance of blends 1,4,5 and 6 are particularly good. These results illustrate the unexpected combinations as benefits in performance.

#### Example 3

Example 1 is repeated by replacing component (b) (polyvinyl alcohol-co-vinyl acetate) by poly-(hydroxyethyl methacrylate) (HEMA). Component (c) (polyethylene-co-vinyl acetate) is replaced by polymethyl methacrylate.

The resulting injection molded polymer is tougher and more resistant to humid than unmodified starch polymer.

#### Example 4

Example 1 is repeated by replacing component (b) (polyvinyl alcohol-co-vinyl acetate) by poly-(hydroxyethyl methacrylate) (HEMA). Polyethylene-co-vinyl acetate (86 % ethylene, 14 % vinyl acetate) is used as component (c). The resulting injection molded polymer is tougher and more resistant to humid air than unmodified starch polymer.

#### Example 5

Example 1 is repeated by increasing component b) to 850 g and replacing component c) by 85 g of polystyrene. The resulting injection molded polymer is tougher and more resistant to humid air than unmodified starch polymer.

#### Example 6

Example 1 is repeated by increasing component b) to 1700 g and replacing component c) by 42 g of polyvinyl chloride-co-vinyl acetate (91 % vinyl chloride - 9 % vinyl acetate). The resulting injection molded polymer is tougher and more resistant to humid air than unmodified starch polymer.

#### Example 7

Example 1 is repeated by replacing component (b) polyvinyl alcohol-co-vinyl butyral (40 % vinyl alcohol, 60 % vinyl butyral). Component (c) is replaced by 42 g polyvinyl butyral. The resulting injection molded polymer is tougher and more resistant to humid air than unmodified starch polymer.

#### Example 8

Example 1 is repeated by increasing component b) to 3400 g and replacing component b) by 38 g polypropylene. The resulting injection molded polymer is tougher and more resistant to humid air than unmodified starch polymer.

#### Example 9

(a) 9500 g of potato starch containing 15.1 % water were placed in a high speed mixer and 425 g of polyvinyl alcohol-co-vinyl acetate (component b) sold as Airvol 540S by Air Products and containing 11 - 13 % of the monomeric units as vinyl acetate and 87 - 89 % of the monomeric units as vinyl alcohol. 80.75 g of hydrogenated fat (lubricant release agent) sold as Boeson VP by Boehringer Ingelheim, 40.37 g of a melt flow accelerator (lecithin) sold as Metarin P by Lucas Meyer were added under stirring. The water content of the final mixture was 14.43 %.

(b) 10,000g of the mixture prepared under (a) were fed through a hopper into a Werner & Pfleiderer co-rotating twin screw extruder (model Continua 37).

The temperature profile of the four sections of the barrel was respectively 20 °C/ 180 °C/ 180 °C/ 80 °C.

Extrusion was carried out with a mixture output of 8 kg/hr (screw speed 200 rpm). Water was added at the inlet with a flow rate of 2 kgs/hr. The water content of the material during extrusion was therefore 31.5 %. In the last section of the extruder 80 mbar reduced pressure was applied to remove part of the water as water vapour.

The water content of the granulates was 17.15 % as measured after they had equilibrated at room temperature.

(c) The granulates of the pre-blended mixture as obtained under (b) (H<sub>2</sub>O content: 17.5 %) were fed through a hopper to an injection molding machine Arburg 329-210-750 for the production of tensile test pieces. The temperature profile of the barrel was: 90 °C/ 165 °C/ 165 °C/ 165 °C.

The shot weight was 8g, the residence time 450 sec., the injection pressure 2082 bar, the back pressure 80 bar, the screw speed 180 rpm.

The tensile test pieces thus produced were conditioned in a climatic cabinet at 50 % R.H. for five days as an arbitrary standard condition.

The test pieces were of standard DIN design (DIN No. 53455).

(d) The conditioned tensile test pieces were then tested for their stress/strain behaviour on a Zwick tensile test apparatus.

The samples were measured at room temperature using an extension rate of 10 mm per minute. Results are presented in Table 3 and compared with those obtained with tensile test pieces obtained from the same starch processed in a similar way but in absence of components b) and c).

Table 3

	unblended starch	Example Nos.								
		9	10	11	12	13	14	15	16	17
break strain %	22	38.5	56	26	33	37	27	43	55	43
break energy KJ/m <sup>2</sup>	325	506	900	338	444	520	315	499	687	500

#### Example 10

(a) 8000 g of potato starch containing 15 % water were placed in a high speed mixer and 2720 g of polyvinyl alcohol-co-vinyl acetate (component b) sold as Airvol 540S by Air Products and containing 11 - 13 % of the monomeric units as vinyl acetate and 87 - 89 % of the monomeric units as vinyl alcohol; 68 g of hydrogenated fat (lubricant release agent) sold as Boeson VP by Boehringer Ingelheim, 34 g of a melt flow accelerator (lecithin) sold as Metarin P by Lucas Meyer were added under stirring. The water content of the final mixture was 15.6 %.

(b) 10,000g of the mixture prepared under (a) were fed through a hopper into a Werner & Pfleiderer co-rotating twin screw extruder (model Continua 37).

The temperature profile of the four sections of the barrel was respectively 20 °C/ 50 °C/ 100 °C/ 50 °C. Extrusion was carried out with a mixture output of 8 kg/hr (screw speed 200 rpm). Water was added at the inlet with a flow rate of 1 kg/hr. The water content of the material during extrusion was therefore 25 %. In the last section of the extruder 22 mbar reduced pressure was applied to remove part of the water as water vapour.

The water content of the granulates was 14.8 % as measured after they had equilibrated at room temperature. They were brought to a water content of 17 % by spraying water under stirring in a conventional mixer.

(c) The granulates of the pre-blended mixture as obtained under (b) (H<sub>2</sub>O content: 17 %) were fed through a hopper to an injection molding machine Arburg 329-210-750 for the production of tensile test pieces. The temperature profile of the barrel was: 90 °C/ 185 °C/ 185 °C/ 185 °C.

The shot weight was 7.9 g, the residence time 450 sec., the injection pressure 2200 bar, the back pressure 80 bar, the screw speed 180 rpm.

The tensile test pieces thus produced were conditioned in a climatic cabinet at 50 % R.H. for five days as an arbitrary standard condition to equilibrate them at a water content of about 14 %.

The test pieces were of standard DIN design (DIN No. 53455).

(d) The conditioned tensile test pieces were then tested for their stress/strain behaviour on a Zwick tensile test apparatus as given in Example 9.

#### Example 11

(a) 8900 g of potato starch containing 15.1 % water were placed in a high speed mixer and 765 g of polyvinyl alcohol-co-vinyl acetate (component b) sold as Airvol 540S by Air Products (containing 11 - 13 mole % vinyl acetate and 87 - 89 mole % vinyl alcohol). 85 g polyethylene-co-vinyl acetate (component c)) containing 20 mole % vinyl acetate and 80 mole % ethylene) sold as Escorene U102020 by Exxon; 85 g polyethylene (component c)) sold as Lupolen 2410T by BASF. 75.65 g of hydrogenated fat (lubricant/release agent) Boeson VP and 37.82 g of a melt flow accelerator (lecithin/Metarin P) were added under stirring. The water content of the final mixture was 13.5 %.

(b) 9000 g of the mixture prepared under (a) were fed through a hopper into the same twin-screw co-rotating extruder described in Example 9. The extrusion of the mixture was carried out with the same temperature profile: 20 °C/ 180 °C/ 180 °C/ 80 °C. The other parameters of the extrusion experiment were the following:

material output: 9 kg/hr  
screw speed: 200 rpm  
water added: 2 kg/hr  
reduced pressure (last section) 300 mbar  
water-content during extrusion: 29.2 %

The water content of the granulates was 17.12 % as measured after they had equilibrated at room temperature.

(c) The granulates obtained under (b) were processed using the same injection molding machine described in (c) of Example 9. The temperature profile of the barrel was 90 °C/ 165 °C/ 165 °C/ 165 °C. The other processing parameters were:

shot weight: 8 g  
residence time: 450 sec.  
injection pressure: 1825 bar  
back pressure: 80 bar  
screw speed: 180 rpm

The tensile test pieces thus produced were conditioned and tested on a Zwick tensile test apparatus as described in (d) of Example 9.

Results are presented in Table 3.

### Example 12

(a) 8900 g of potato starch containing 15.5 % water were placed in a high speed mixer and 765 g of polyvinyl alcohol-co-vinyl acetate (component b) containing 11 - 14 mole % vinyl alcohol and 87 - 89 mole % vinyl acetate; 170 g of polyamide-block-polyether (component c) sold as Pebax MA-4011 by Atochem; 75.65 g of hydrogenated fat (lubricant/ release agent) Boeson VP; 37.82 g of a melt flow accelerator (lecithin) Metarin P were added under stirring. The water content of the final mixture was 13.4 %.

(b) 9000 g of the mixture prepared under (a) were fed through a hopper into the same twin-screw co-rotating extruder described in Example 9.

The extrusion of the mixture was carried out with the following processing parameters:

temperature profile: 20 °C/ 220 °C/ 220 °C/ 80 °C

material output: 8 kg/hr

screw speed: 200 rpm

water added: 2 kg/hr

reduced pressure (last section): 150 mbar

water content during extrusion: 29.14 %

The water content of the granulates was 17.20 % after they had equilibrated at room temperature.

(c) The granulates of (b) were processed using the same injection molding machine of Example 9. The processing parameters were the following:

temperature profile: 90 °C/ 165 °C/ 165 °C/ 165 °C

shot weight: 8 g

residence time: 450 sec

injection molding: 2220 bar

back pressure: 80 bar

screw speed: 180 rpm

The tensile test pieces thus produced were conditioned and tested on a Zwick tensile test apparatus described in (d) of Example 9.

Results are presented in Table 3.

### Example 13

(a) 8900 g of potato starch containing 15.1 % water were placed in a high speed mixer and 765 g of polyvinyl alcohol-co-vinyl acetate (component b) Airvol 540S and containing 11 - 13 mole % of vinyl alcohol and 87 -89 mole % vinyl acetate; 170 g of a thermoplastic elastomer polyurethane block polyether (component c) sold as Pellethane 2103-80-AE by Dow Chemical Company; 75.65 g of hydrogenated fat (lubricant/ release agent) Boeson VP; 37.82 g of a melt flow accelerator (lecithin) Metarin P were added under stirring. The water content of the final mixture was 13.5 %.

(b) 9000 g of the mixture prepared under (a) were fed through a hopper into the same twin-screw co-rotating extruder described in Example 9.

The extrusion of the mixture was carried out with the following processing temperature:

temperature profile: 20 °C/ 220 °C/ 220 °C/ 80 °C

material output: 8 kg/hr

screw speed: 200 rpm

water added: 2 kg/hr

reduced pressure (last section): 80 mbar

water content during extrusion: 29.2 %

The water content of the granulates was 16.9 % after they had equilibrated at room temperature.

(c) The granulates obtained under (b) were processed using the same injection molding machine described in (c) of Example 9. The processing parameters were the following:

temperature profile: 90 °C/ 165 °C/ 165 °C/ 165 °C

shot weight: 8 g

residence time: 450 sec

injection molding: 2220 bar

back pressure: 80 bar

screw speed: 180 rpm

The tensile test pieces thus produced were conditioned and tested on a Zwick tensile test apparatus described in (d) of Example 9.

Results are presented in Table 3.

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#### Example 14

(a) 8000 g of potato starch containing 15.1 % water were placed in a high speed mixer and 340 g of polyvinyl alcohol-co-vinyl acetate, Airvol 540S (component b) containing 11 - 13 mole % of vinyl alcohol and 87 - 89 mole % vinyl acetate; 680 g of polyamide block polyether thermoplastic elastomer (component c) sold as Pebax MA-4011 by Atochem; 680 g of polyurethane-block-polyether thermoplastic elastomer (component c) sold as Pellethane 2103-80-AE by Dow Chemical Company; 68 g of hydrogenated fat (lubricant/ release agent) Boeson VP; 34 g of a melt flow accelerator (lecithin) Metarin P were added under stirring. The water content of the final mixture was 12.3 %.

(b) 9000 g of the mixture prepared under (a) were fed through a hopper into the same twin-screw co-rotating extruder described in Example 9.

The extrusion of the mixture was carried out with the following processing parameters:

temperature profile: 20 °C/ 220 °C/ 220 °C/ 80 °C

material output: 8 kg/hr

screw speed: 200 rpm

water added: 2.1 kg/hr

reduced pressure (last section): 600 mbar

water content during extrusion: 27.7 %

The water content of the granulates was 16.8 % after they had equilibrated at room temperature.

(c) The granulates obtained under (b) were processed using the same injection molding machine described in (c) of Example 9. The processing parameters were the following:

temperature profile: 90 °C/ 165 °C/ 165 °C/ 165 °C

shot weight: 8 g

residence time: 450 sec

injection molding: 1650 bar

back pressure: 80 bar

screw speed: 180 rpm

The tensile test pieces thus produced were conditioned and tested on a Zwick tensile test apparatus described in (d) of Example 9.

Results are presented in Table 3.

#### Example 15

Example 14 was repeated with the differences that (i) potato starch was decreased to 5000 g, (ii) polyvinyl alcohol-co-vinyl acetate (Airvol 540S) was increased to 1770 g, (iii) polyamide (Pebax-4011) was decreased to 531 g and (iv) the polyurethane (Pellethane 2103-80-AE) was decreased to 531 g.

Results are given in Table 3.

45

#### Example 16

(a) 7000 g of potato starch containing 15.0 % water were placed in a high speed mixer and 1700 g of polyvinyl alcohol-co-vinyl acetate (component b) Airvol 540S (component b) containing 11 - 13 mole % of vinyl acetate and 87 - 89 mole % vinyl alcohol (Airvol 540S); 425 g of a thermoplastic elastomer polyamide-block-polyether Pebax Ma-4011 of Atochem; 425 g of thermoplastic elastomer polyurethane-block-polyether Pellethane 2103-80-AE by Dow Chemical Company; 59.5 g of hydrogenated fat (lubricant/ release agent) Boeson VP; 29.75 g of a melt flow accelerator (lecithin) Metarin P were added under stirring. The water content of the final mixture was 11 %.

(b) 9000 g of the mixture prepared under (a) were fed through a hopper into the same twin-screw co-rotating extruder described in Example 9.

The extrusion of the mixture was carried out with the following processing parameters:

temperature profile: 20 ° C; 220 ° C; 220 ° C; 80 ° C

material output: 8 kg/hr

screw speed: 200 rpm

water added: 2.1 kg/hr

5 reduced pressure (last section): 600 mbar

water content during extrusion: 26.8 %

The water content of the granulates was 16.8 % after they had equilibrated at room temperature.

(c) The granulates obtained under (b) were processed using the same injection molding machine described in (c) of Example 9. The processing parameters were the following:

10 temperature profile: 90 ° C; 165 ° C; 165 ° C; 165 ° C

shot weight: 8 g

residence time: 450 sec

injection molding: 2280 bar

back pressure: 80 bar

15 screw speed: 180 rpm

The tensile test pieces thus produced were conditioned and tested on a Zwick tensile test apparatus described in (d) of Example 9.

Results are presented in Table 3.

20

#### Example 17

(a) 5000 g of potato starch containing 15.0 % water were placed in a high speed mixer and 708 g of polyvinyl alcohol-co-vinyl acetate, Airvol 540S (component b) containing 11 - 13 mole % of vinyl alcohol and 87 - 89 mole % vinyl acetate (Airvol 540S); 2125 g of a polyethylene-co-vinyl alcohol EVAL EP-L-101 (component c)) containing 73 mole % vinyl alcohol and 27 mole % ethylene; 42.5 g of hydrogenated fat (lubricant/ release agent) Boeson VP; 21.3 g of a melt flow accelerator (lecithin) Metarin P were added under stirring. The water content of the final mixture was 9.8 %.

(b) 9000 g of the mixture prepared under (a) were fed through a hopper into the same twin-screw co-rotating extruder described in Example 9.

The extrusion of the mixture was carried out with the following processing parameters:

temperature profile: 20 ° C; 80 ° C; 220 ° C; 180 ° C

material output: 8 kg/hr

screw speed: 200 rpm

35 water added: 2.1 kg/hr

reduced pressure (last section): 33 mbar

water content during extrusion: 28.7 %

The granulates were brought to a water content of 17 % by spraying water under stirring in a conventional mixer.

(c) The granulates obtained under (b) were processed using the same injection molding machine described in (c) of Example 9. The processing parameters were the following:

temperature profile: 90 ° C; 175 ° C; 175 ° C; 175 ° C

shot weight: 7.6 g

residence time: 450 sec

45 injection molding: 2020 bar

back pressure: 80 bar

screw speed: 180 rpm

The tensile test pieces thus produced were conditioned and tested on a Zwick tensile test apparatus described in (d) of Example 9.

50 Results are given in Table 3.

#### Example 18

55 Example 1 (Sections a) and b)) is repeated except that the water content is adjusted to 22 %, and the cutter is removed from the die face. A continuous extrudate is obtained which is foamed as a result of the excess water evaporation. The foam is chopped into 30-40 mm lengths and is useful as a loose-fill, packaging insulation material.

Example 19

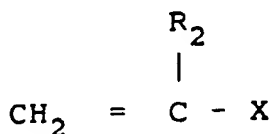
During each of the injection molding operations in Examples 2 - 14 an experiment is performed to demonstrate the utility of making foams. The molten material was obtained as described in Example 1, Sections a), b) and c) in each case was extruded into the open atmosphere (Section c) instead of being injection molded into a closed mold. In every case the material is converted into a foamed extrudate useful for loose-fill in packaging applications.

10 Example 20

The granulates from Example 1 are mixed with polystyrene in the proposition of 30 to 70 parts by weight and are treated according to Example 18. The resulting foamed extrudate contains a very fine and uniform all structure suitable for a variety of uses including structural foam.

15 Claims

1. A composition of matter capable of being formed into articles having substantial dimensional stability comprising
  - a) destructured starch, and
  - b) at least one polymer which contains at least two different types of functional groups, one of said types being hydroxyl groups, said polymer being present in an amount effective to enhance the physical properties of said articles.
2. The composition according to claim 1 wherein the polymer of component b) contains vinyl alcohol units.
3. The composition according to claim 2 wherein the polymer of component b) is a poly(vinyl ester) wherein the ester groups are partially hydrolyzed.
4. The composition according to claim 2 wherein the polymer of component b) is a copolymer containing vinyl alcohol units as well as other units as are obtained by polymerization of vinyl esters with one or more monomers selected from the group consisting of ethylene, vinyl chloride, vinyl ethers, acrylonitrile, acryl amide, omega-octadecene, vinyl butyl ether, vinyl-octadecyl ether, vinyl pyrrolidone and other known monomers, with subsequent hydrolysis of at least some of the vinyl-ester groups.
5. The composition according to claim 4 wherein the copolymer of component b) is selected from the group consisting of poly(vinyl alcohol-co-vinylacetate), ethylene/vinyl alcohol/ vinyl acetate copolymers, ethylene/vinyl chloride/vinyl alcohol/vinyl acetate graft copolymers, vinyl alcohol/vinyl acetate/vinyl chloride copolymers, vinyl alcohol/vinyl acetate/vinyl chloride/diacryl amide copolymers, vinyl alcohol/vinyl butyral copolymers, vinyl alcohol/vinyl acetate/vinyl pyrrolidone copolymers, and mixtures or combinations thereof.
6. The composition according to claim 4 wherein the polymer of component b) is a copolymer as obtained by polymerization of a vinyl ester with one or more monomers selected from the group consisting of ethylene, vinyl ethers, with subsequent hydrolysis of at least some of the vinyl ester groups.
7. A composition according to claim 1 wherein component b) is a polymer or a copolymer as obtained from polymerizing or copolymerizing monomers: of the formula



wherein R<sub>2</sub> is hydrogen or methyl; and X is an organic moiety with up to 8 carbon atoms substituted by 1 to 3 hydroxyl groups and/or containing 1 or 2 carboxylate groups and does not form a vinyl alcohol or of an ester derivative of maleic acid or fumaric acid which optionally contain hydroxyl groups.

8. A composition according to claim 7 wherein component b) is a polymer or a copolymer of one or more compounds of the formula CH<sub>2</sub>=C(R<sub>2</sub>)X<sub>1</sub>, wherein X<sub>1</sub> is -CH<sub>2</sub>OH, -O-CH<sub>2</sub>-CH<sub>2</sub>-OH, -C(O)OCH<sub>2</sub>-CH<sub>2</sub>OH or -C<sub>6</sub>H<sub>4</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>OH, and/or of a compound of the formula

$\text{HOCH}_2\text{-CH}_2\text{-O(O)C-HC} = \text{HC-C(O)O-CH}_2\text{-CH}_2\text{OH}$   
(cis or trans)

9. A composition according to claim 7 wherein the polymer of component b) is a copolymer of a monomer of a compound of formula  $\text{CH}_2 = \text{C(R}_2\text{)X}$  or said derivatives of maleic or fumaric acid copolymerized with one or more vinyl esters, ethylene, vinyl chloride, vinyl esters, acrylonitrile, methacrylic acid esters, maleic acid esters, acrylamide, omega-octadecene, vinyl butyl ether, vinyl-octadecyl ether, vinyl pyrrolidone and other known monomers.

10. A composition according to claim 9 wherein the weight % of the hydroxyl moiety (-OH) is from 4.5 to 35 weight percent of the component b).

11. The composition according to claim 1 wherein the weight % ratio of destructurized starch to component b) is about 1:99 to about 99:1, preferably wherein destructurized starch is present in amounts of about 50 % to about 99 % by weight of the total composition.

12. The composition according to anyone of the claims 1 to 11 wherein there is additionally incorporated component c) comprising an substantially water-insoluble thermoplastic polymer which does not fall within the definition of those compounds defined as component b).

13. The composition according to claim 12 wherein said component c) is selected from the group consisting of polyolefines, vinyl polymers, polystyrenes, polyacrylonitriles, poly(vinyl carbazols), polyacrylates, polymethacrylates, polyacetals, thermoplastic polycondensates, polyarylethers, thermoplastic polyimides, high molar-mass substantially water-insoluble or crystallizable poly(alkylene oxides), and mixtures thereof.

14. The composition of claim 13 wherein component c) is selected from the group consisting of polyethylenes, polypropylenes, polyisobutylenes, ethylene oxide polymers, propylene oxide polymers, polystyrene and mixtures thereof.

15. The composition of claim 13 wherein component c) is selected from the group consisting of poly(vinyl chlorides), poly(vinyl acetate), polyamides, thermoplastic polyesters, thermoplastic polyurethanes, polycarbonates, poly(alkylene terephthalates) and mixtures thereof.

16. The composition according to claim 12 wherein component c) is selected from the group consisting of alkylene/vinyl ester-copolymers, alkylene/acrylate or methacrylate copolymers, ABS copolymers, styrene/acrylonitrile copolymers, alkylene/maleic anhydride copolymers, partially hydrolyzed polyacrylates or polymethacrylates, partially hydrolyzed copolymers of acrylates and methacrylates, acrylic acid esters/acrylonitrile copolymers and hydrolysates thereof, acrylamide/acrylonitrile copolymers and mixtures thereof.

17. The composition according to claim 16 wherein component c) is selected from the group consisting of ethylene/vinyl acetate copolymers (EVA), ethylene/vinyl alcohol copolymers (EVAL), ethylene/acrylic acid copolymers (EAA), ethylene/ethyl acrylate copolymers (EEA), ethylene/methacrylate copolymers (EMA), styrene/acrylonitrile copolymers (SAN), ethylene/maleic anhydride copolymers and mixtures thereof.

18. The composition according to anyone of the claims 12 to 17 wherein the sum of components b) and c) constitute about 1% to about 99%, preferably about 20% to about 80% and preferably about 1% to about 30% by weight of the total composition.

19. The composition according to anyone of the claims 1 to 18 wherein the destructurized starch has a water content of about 5% to about 40% and preferably of about 10% to about 22% by weight of the total starch content.

20. The composition according to anyone of the claim 1 or 19, wherein there are additionally incorporated one or more materials selected from the group consisting of adjuvants, fillers, lubricants, mold release agents, plasticizers, foaming agents, stabilizers, extenders, chemical modifiers, flow accelerators, coloring agents, pigments and mixtures thereof.

21. The composition according to anyone of the claims 1 to 20 further containing an agriculturally active compound.

22. The composition according to anyone of the claims 1 to 21 which is a melt blend.

23. The composition according to anyone of the claims 1 to 21 which is a cooled solidified blend.

24. The composition according to claim 23 in particulate, granulated or pelletized form.

25. A thermoplastic destructurized-starch product having substantial dimensional stability, made from a composition as claimed in anyone of the claims 1 to 21, formed by the process comprising:

1) providing a mixture comprising starch and at least one polymer which contains at least two different types of functional groups, one of said types being hydroxyl groups (component b);

2) heating said mixture in a closed volume under sufficient temperature and pressure for a time long enough to effect destructurization of said starch and form a substantially homogenous melt;

3) shaping said melt into an article; and



- 4) allowing said shaped article to cool to a substantially dimensionally stable thermoplastic product.
26. The product according to claim 25 wherein destructurization of the starch is carried out at a temperature above its melting point and glass transition temperature.
27. The product according to claim 26 wherein the destructurization of the starch is carried out at temperatures of about 105 °C to about 240 °C and preferably at temperatures of about 130 °C to about 190 °C.
28. The product according to anyone of the claims 25 to 27 wherein the melt is formed under the range of pressure from the minimum pressure necessary to avoid formation of water vapour under the applied temperature up to about  $150 \times 10^5 \text{ N/m}^2$ .
29. The product according to anyone of the claims 25 to 28 wherein the heat and pressure are maintained until the starch has undergone the specific narrow endothermic transition just prior to its endothermic change characteristic of oxidative and thermal degradation.
30. The product according to anyone of the claims 25 to 28 which is a granulate, a pellet or a powder.
31. The product according to anyone of the claims 25 to 28 in the form of a shaped article selected from the group consisting of containers, bottles, pipes, rods, packaging material, sheets, foams, films, sacks, bags and pharmaceutical capsules.
32. The product according to claim 30 further melted and processed to form a shaped article selected from the group consisting of containers, bottles, pipes, rods, packaging material, sheets, foams, films, sacks, bags and pharmaceutical capsules.
33. The shaped articles according to claims 31 and 28, wherein the shaping process comprises foaming, filming, compression molding, injection molding, blow molding, extruding, co-extruding, vacuum forming, thermoforming and combinations thereof.
34. A thermoplastic destructurized-starch substantially homogenous melt, made from a composition as claimed in anyone of the claims 1 to 21, formed by the process comprising:
- 1) providing a mixture comprising starch and at least one polymer which contains at least two different types of functional groups, one of said types being hydroxyl groups (component b); and
  - 2) heating said mixture in a closed volume under sufficient temperature and pressure for a time long enough to destructurize said starch and form said melt.
35. The melt according to claim 34 wherein destructurization of the starch is carried out at a temperature above its melting point and glass transition temperature.
36. The melt according to claim 34 wherein destructurization of the starch is carried out at a temperature of about 105 °C to about 240 °C, preferably at a temperature of about 130 °C to about 190 °C.
37. The melt according to anyone of the claims 34 to 36, wherein the melt is formed under the range of pressure from the minimum pressure necessary to avoid formation of water vapour under the applied temperature up to about  $150 \times 10^5 \text{ N/m}^2$ .
38. The melt according to claim 37 wherein the heat and pressure are maintained until the starch has undergone the specific narrow endothermic transition just prior to its endothermic change characteristic of oxidative and thermal degradation.
39. The melt according to anyone of the claims 34 to 38 wherein said provided mixture additionally contains component c) comprising an substantially water- insoluble thermoplastic polymer which does not fall within the definition of those compounds defined as component b).



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(54) **Polymer base blend compositions containing destructured starch.**

(57) A thermoplastic polymer composition comprising  
a) a destructured starch, and  
b) an effective amount of at least one polymer  
which contains at least two different types of  
functional groups, one of said types of these  
groups being hydroxyl groups.

The composition may contain further conventional additives as well as hydrophobic, substantially water-insoluble polymers.

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## EUROPEAN SEARCH REPORT

Application Number

EP 90 81 0434

### DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	IND. ENG. CHEM. PROD. RES. DEV., vol. 23, 1984, pages 594-595; B.T. NWUTO et al.: "Extrusion of starch-extended water-soluble polyvinyl alcohol" * Page 595, table III * - - - -	1-39	C 08 L 3/02 C 08 L 57/10 C 08 L 29/00 // (C 08 L 3/02 C 08 L 29:04 C 08 L 23:08 ) (C 08 L 3/02 C 08 L 33:14 C 08 L 33:12 )
Y	GB-A-2 190 093 (WARNER-LAMBERT) * Page 2, lines 56-57; claims * - - - -	1-39	
E	EP-A-0 400 532 (BUTTERFLY) * The whole document * - - - - -	1-39	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 L
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
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